



Evaluation of Cu- and CuZn-Exsolved Catalysts for the CO₂ Hydrogenation to MeOH

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Significance and Relevance

Developing highly active and stable methanol synthesis catalysts is essential for transitioning from CO to CO₂ as carbon source in industrial applications promoting greener decarbonisation solutions. In this work, novel CO₂-to-methanol catalysts have been developed through the *exsolution* approach and benchmarked against the state-of-the-art commercial material. The new materials showed extremely high stability to deactivation and coarsening, as well as the dual formation of MeOH and DME, highlighting their potential as new generation catalysts for the CO₂ hydrogenation to MeOH reaction.

Preferred and 2nd choice for the topic: CO₂ utilization and recycling

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Among the most promising approaches to reduce CO₂ emissions through chemical valorization strategies, the CO₂ catalytic conversion to methanol (MeOH), a widely usable component for fuels, plastic, paints, chemicals, and a building block for more complex fuels, is considered an extremely promising strategy. Despite the growing interest in its industrial implementation, a major challenge related to this process is the low CO₂ conversion, triggered by limited catalyst selectivity and deactivation by active metal nanoparticle (NP) sintering. Recent works on materials improvement for efficient, stable and selective hydrogenation of CO₂ to MeOH have highlighted Cu-and-ZnO-based catalysts as among the most promising materials for this application.^{1,2} However, even considering the state-of-the-art Cu/ZnO/Al₂O₃ commercial catalyst, problems arise from i) kinetic limitations when using CO₂ instead of CO as feed, ii) Cu instability, given its high mobility and proneness to sintering in operating conditions, and iii) low CO₂/H₂O tolerance.³ The design of new catalysts with improved activity and stability is, hence, a key ambition in the field. In this work, the development of optimised catalysts for CO₂ conversion to MeOH using the novel approach of 'exsolution'⁴ has been carried out. To obtain this, a solid solution incorporating Cu as ion into the 'host' structure was synthesised, followed by the *in situ* formation of surface metallic nanoparticles (NPs) through controlled reduction. After such NP exsolution, the samples were tested at relevant conditions for the CO₂ hydrogenation to MeOH to assess the newly developed catalysts' stability, activity and selectivity.

Materials and Methods

Spinel pure-phase materials were prepared by co-precipitation of nitrate precursors (Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Cu(NO₃)₂·3H₂O) in an NH₃ solution, followed by product separation and drying, and then calcined and sintered in air (T=700-850 °C). The exsolution of the as-synthesised samples was investigated in 5% H₂/N₂ at temperatures ranging between 350-550 °C and times between 4-10 h. Catalytic tests were carried out in a fixed-bed reactor at 23 barg pressure and temperatures ranging from 180-300 °C. To rationalise the catalytic performance of the different materials, all samples (pre- and post-exsolution and post-catalytic testing) were characterised by N₂ physisorption, XRD, H₂-TPR, CO₂-TPD, XPS, SEM, TEM, and STEM-EDX spectroscopy.

Results and Discussion

Characterisation of specific surface area (BET), affinity for CO₂ (CO₂ TPD), and surface species obtained (XPS) allowed to identify the best candidates for the investigated reaction before testing at operating pressure (23 barg) in the test rig. The results showed successful exsolution of both Cu-metal only and CuZn-alloy NPs after reduction at different conditions of temperatures, times, and humidity. The main differences among the investigated samples were found in the size of the exsolved NPs and the amount

of depleted dopant, mainly dependent on the reduction time. Instead, the reduction temperatures chosen determined the NPs' composition, with lower T being responsible for single-metal exsolution, as opposed to alloy exsolution at higher T, for the same starting composition. For all investigated samples, the exsolution strategy, thanks to the strong anchorage of the exsolved NPs to the spinel ($\text{CuZnAl}_2\text{O}_4$) host and the strain imposed by the NPs at the support interface by their unique “socketing” (*i.e.*, anchorage), maximised the Cu/CuZn-spinel interaction and stabilised the NPs on the surface of the oxide support, even after ~ 50 h of testing ($3\text{H}_2\text{:CO}_2$, 20 NL/h, 23 barg, 180-300 °C). A maximum CO_2 conversion of $\sim 17\%$ was achieved for the best-performing samples, very close to the calculated thermodynamic equilibrium (Fig. 1a). When compared to the commercial catalyst ($\text{Cu/ZnO/Al}_2\text{O}_3$), the exsolved samples showed a much higher space-time yield (STY, $\text{mmol}_{\text{MeOH}} \text{g}_{\text{Cu}}^{-1} \text{h}^{-1}$), as shown in Figure 1b. Interestingly, dimethyl ether (DME) was detected as reaction product for all samples, as well as MeOH and CO, with the highest selectivity towards MeOH obtained at 200 °C (76%), as reported in Figure 1c. All the exsolved samples showed enhanced stability, with post-catalytic test characterisation showing no sintering/coalescence of the exsolved NPs, as demonstrated by the STEM-EDX comparison in Figure 1 d-e for the same sample pre- and post-catalytic testing, respectively.

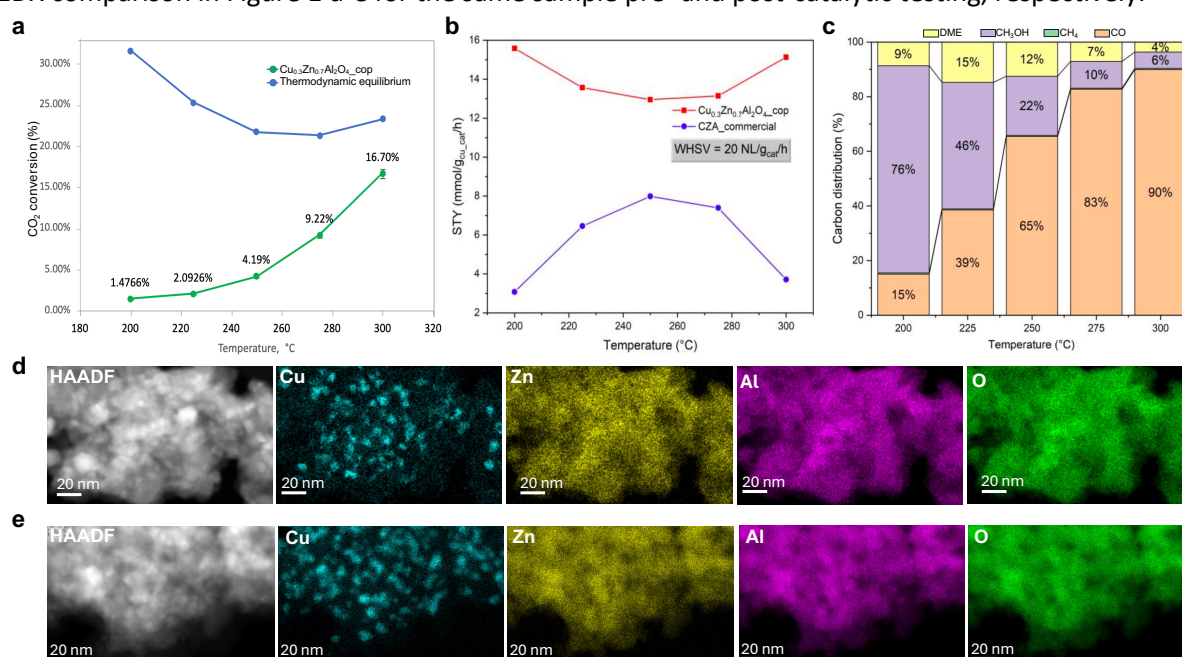


Figure 1. a) CO_2 conversion of the best performing exsolved spinel sample showing $\sim 17\%$ conversion at 300 °C; b) STY comparison for the best performing exsolved sample vs. the commercial $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst; c) product distribution obtained for tests at $T=200\text{--}300$ °C with DME production at all temperatures; d) STEM-EDX characterisation of an exsolved $\text{Cu}_{0.3}\text{Zn}_{0.7}\text{Al}_2\text{O}_4$ catalyst before and d) after ~ 50 h of continuous testing ($T=200\text{--}300$ °C; $P=23$ barg) showing high stability of the exsolved NPs which retained their size and density distribution.

Building upon proven compositions of state-of-the-art catalysts, this work highlights the potential of new exsolved catalysts for the efficient catalytic CO_2 hydrogenation to MeOH. Specifically, the results obtained in this work open the possibility of overcoming some of the challenges hindering the implementation of such catalytic processes at industrial level, potentially advancing the technology of MeOH synthesis catalysts through achieving high activity *and* stability.

References

1. T. A. Atsbha, *et al.*, *J. CO₂ Util.* **2021**, 44, 101413.
2. Y. Liu, *et al.*, *ACS Catal.* **2024**, 14, 12610–12622.
3. S. Navarro-Jaen, *et al.*, *Nat. Rev. Chem.* **2021**, 5, 564.
4. Calì, E., *et al.*, *Nature Commun.* **2023**, 14(1), 1754.

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